Polymer Systems and Film Formation Mechanisms in High Solids, Powder, and UV Cure Systems

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Film Formation in Coatings

Outline:

- Thermoplastic systems
- Thermosetting systems
- Variables controlling property development
- Stages of property development
- Waterborne
- Energy cure
- Powder coating
Almost all desirable properties of a coating film strongly depend upon the quality and integrity of the coating film which in turn depends upon the polymer chemistry, formulation variables, the $T_g$ of the dry film and the surface characteristics of the substrate among other factors.
Coating properties influenced by film formation process

Adhesion
Chemical resistance
Mechanical properties
Dirt pick up
Flow
Gloss
Pop (blister)
Sag
Surface dry and hardness development
Film Formation

Three major classification of film formers

- Thermoplastic materials
- Chemically converting systems
- Latex systems
Chemical and Physical Variables Controlling Property Development

Molecular weight
Crosslink Density
Glass Transition Temperature
Building blocks
Viscosity
Cure Temperature
Formulation variables
<table>
<thead>
<tr>
<th>Property</th>
<th>Thermoplastic</th>
<th>Thermoset</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW prior to application</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>MW as dry film</td>
<td>High</td>
<td>Very high</td>
</tr>
<tr>
<td>Crosslink density</td>
<td>Very low</td>
<td>Moderate-v.high</td>
</tr>
<tr>
<td>Hardness</td>
<td>Poor-good</td>
<td>Moderate-Excellent</td>
</tr>
<tr>
<td>Solvent resistance</td>
<td>Poor-good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>Poor-Excellent</td>
<td>Moderate-Excellent</td>
</tr>
<tr>
<td>Permeability, H$_2$O</td>
<td>Very low-high</td>
<td>Very low</td>
</tr>
<tr>
<td>Gloss</td>
<td>Low-high</td>
<td>High-very high</td>
</tr>
<tr>
<td>Recoatability</td>
<td>Excellent</td>
<td>Poor-good</td>
</tr>
<tr>
<td>Low VOC use</td>
<td>Poor</td>
<td>Excellent</td>
</tr>
</tbody>
</table>
Some Milestones:

• A Film is dry-to-touch when viscosity is $>10^3$ Pa.s

• To resist blocking for 2s at 20 Psi, need viscosity $>10^7$ Pa.s

• To serve as industrial enamel, viscosity often must be $>10^{12}$ Pa.s, the viscosity at Tg.
Film Formation

Relationship between viscosity and temperature

\[
\ln \eta = 27.6 - \frac{40.2 \cdot (T - T_g)}{51.6 + (T - T_g)}
\]

T, in Kelvin-degrees

Williams, Landel and Ferry (WLF) Equation
Thermoplastic Systems

Polymer chains are longer but remain separate. Though they may coil around one another and exhibit branching, there is no primary valency bonding between chains.
Film Formation by Evaporation of Solvent from Solutions of Polymers-- Lacquers

- To have good film properties, polymer molecules must be large (very high molecular weight)

However,

- Concentrated solutions of high molecular weight polymers are too viscous. Dilute solutions have high VOC.
Film Formation--Air dry (Lacquer)

High Polymer Solution → Drying → Dry Film → Aging

Solvent Evaporation
Film Formation--Air dry (Lacquer)

The cross chain linkages are weak secondary valency bonds broken relatively easily as the film is dissolved or melted.
Principles of Film Formation

Stages of film formation (High $T_g$)

- At the early stages of drying, the rate of solvent evaporation is essentially independent of the presence of polymer.

- The rate of evaporation depends upon:
  - The vapor pressure
  - The ratio of surface area to volume of the film
  - The rate of air flow
Principles of Film Formation

Stages of Film formation

As the viscosity and $T_g$ increase, free volume decreases, and the rate of solvent evaporation depends on how rapidly the solvent molecules can reach the surface of the film.

The rate of solvent loss is controlled by the rate of DIFFUSION of the solvent through the film.
Principles of Film Formation

Lower $T_g$ and more free-volume available
Solvent evaporates easily
Vapor pressure controlled

Higher $T_g$, and viscosity
Lower free volume
Diffusion controlled
The rate of solvent diffusion and evaporation also depends on the solvent structure and the solvent polymer interaction.

<table>
<thead>
<tr>
<th>CH$_3$COOCH$_2$(CH$_2$)$_2$CH$_3$</th>
<th>CH$_3$COOCH$_2$CH(CH$_3$)$_2$</th>
<th>n-Butyl acetate</th>
<th>Isobutyl acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butyl acetate Diffuses more rapidly</td>
<td>Isobutyl acetate Higher evaporation rate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$ (CH$_2$)$_6$CH$_3$</td>
<td>CH$_3$ (CH$_2$)$_5$CHCH$_3$</td>
<td>n-Octane</td>
<td>Isooctane</td>
</tr>
<tr>
<td>n-Octane</td>
<td>Isooctane</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
# Thermoset Systems

## Chemically reactive systems

<table>
<thead>
<tr>
<th>Main Resin</th>
<th>Cross-linker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyols</td>
<td>Amino Resins</td>
</tr>
<tr>
<td>Polyols</td>
<td>(Poly)isocyanates</td>
</tr>
<tr>
<td>Polycarboxylic acids</td>
<td>Epoxies</td>
</tr>
<tr>
<td>Polycarboxylic acids</td>
<td>Carbodiimides</td>
</tr>
<tr>
<td>Polycarboxylic acids</td>
<td>Aziridines</td>
</tr>
<tr>
<td>(Poly)amines, amides</td>
<td>Epoxies</td>
</tr>
<tr>
<td>Acetoacetate (active methylene)</td>
<td>Amino resins</td>
</tr>
<tr>
<td>Acetoacetate (active methylene)</td>
<td>(Poly)isocyanate</td>
</tr>
<tr>
<td>Polyols and polycarboxylic acids</td>
<td>Siloxanes</td>
</tr>
</tbody>
</table>

Miscellaneous Combinations
The mechanical properties of the film depend strongly upon the $T_g$ of the crosslinked polymer and upon the degree of crosslinking.

Physical properties such as water and oxygen permeability, solvent and chemical resistance are affected by the degree of crosslink density.
A number of extreme changes accompany crosslinking

- Soluble
- Flow
- Glass Transition Temperature

- Insoluble
- Severely reduced flow
- Increase in Tg
Crosslinking

Linear Polymer + Crosslinker → Network (Crosslinked Polymer)
$T_g$ increases during crosslinking for three reasons:

- Chain mobility near crosslinks is constrained
- Crosslinkers are converted from plasticizers to network chain segments
- $M_n$ of main resin increases sharply
Crosslinking requires that the reactants diffuse into a reaction volume.

Small molecules may diffuse more readily than functional groups on a polymer chain.

Water plasticizes coatings, lowering their Tg.
Thermoset Systems

If the diffusion rate is greater than the reaction rate, the reaction will be kinetically controlled.

If the diffusion rate is slow compared to the reaction rate, the rate is mobility controlled.
Thermoset Systems

The major factor controlling rate is the availability of free volume.

The free volume is large if the reaction temperature is higher than the Tg.

If the reaction temperature is below Tg, the free volume is limited.

At intermediate temperatures, the reaction is controlled by the rate of diffusion (*mobility of reactants*).
If the reaction temperature is above the Tg of fully reacted polymer, there will be no mobility effect.

In ambient curing coatings if the Tg of the fully cured polymer is above the ambient, the reaction will become mobility controlled.

As Tg approaches the cure temperature, reaction becomes slower.

When Tg equals T, reactions become very slow and **Vitrification** occurs.
Waterborne

Film Formation in Latex Systems
Film Formation--Waterborne Coatings

Core-Shell Latex

Multiphase Latex

Dispersion

HO
OCN
Epoxy

COOH

Epoxy
Alkyd
Acrylic
Polyester
Polyurethane

Resins

OH
NCO
Epoxy
Film Formation from Latex

Occurs in three overlapping stages

- **Evaporation** of water and co-solvents leading to close packed layers of latex particles

- **Deformation** of the particles from their spherical shape leading to a more or less continuous layer

- **Coalescence**, a relatively slow process in which the polymer particles and molecules interdiffuse across the particle boundaries and tangle, strengthening the film.
What Derives Deformation?

• Capillary forces?
• Powerful (up to 5000 psi) but short lived
• Surface energy reduction?
• Much weaker but longer lived
What Derives Deformation?

$T_g$ of the latex particles is an important factor

- $T_g$ of the outer shell is what counts
- particles and film can be plasticized by water and coalescent agents (solvents)
Film Formation

Top view of the drying latex showing three contacting particles with a capillary full of water in between
Film Formation

Thin layer of water around the particles

Schematic representation of two spheres in contact after partial evaporation of water
Coalescence

For a given latex, the lowest temperature at which coalescence occurs sufficiently to form a continuous cohesive film is called its

Minimum Film Formation Temperature MM FT (MFT)
• Complete coalescence is a slow process

• The rate is affected by \((T-T_g)\)

• Coalescing agents reduce \(T_g\) and MFFT.
Coalescence

• Coalescence occurs as molecules interdiffuse. The distance the molecules travel to interdiffuse is considerably less than the diameter of a typical latex particle

• The rate of interdiffusion is directly related to $T - T_g$. As a broad rule, coalescence will not occur unless the temperature is at least slightly higher than $T_g$. 
Film Formation

Scanning Electron Micrograph of films prepared from a latex polymer
NanoScope Tapping AFM
Scan size 2.000 μm
Setpoint 2.539 N
Scan rate 1.489 Hz
Number of samples 512
Latex Film Formation

Stage I: Water Evaporation
- Aqueous Latex
  - Close-Contact Particles

Stage II: Particles Deform
- Packing of Deformed Particles

Stage III: Coalescence (aging)
- Mechanically Coherent Dry Film
Crosslinking Latex

Fast crosslinking

Weak Boundaries

Weak film interfacial fracture

Polymer Diffusion

Fully diffused

Crosslinked film

Strong film cohesive fracture
Film Formation in Energy Cured Coatings
“Energy” Curing

• “Energy” Curing - initiation by:
  – UV: 200 - 400nm light
  – Visible: typically 380 - 450
  – Electron beam

• Radical mechanism
• Cationic mechanism
Radical Curing Mechanism

**Initiation Step**

\[
\text{R} \quad + \quad \text{O} = \quad \text{O} \quad \rightarrow \quad \text{R} \quad \text{O} = \quad \text{O}
\]

**Propagation**

\[
\text{R} \quad \text{O} = \quad \text{O} \quad + \quad \text{O} = \quad \text{O} \quad \rightarrow \quad \text{R} \quad \text{O} = \quad \text{O} \quad \rightarrow \quad \text{M} \quad \text{O} = \quad \text{O}
\]

**Termination Steps**

\[
\text{M} \quad \bullet \quad \rightarrow \quad \text{M} - \text{M} \quad \text{O} = \quad \text{O} \quad \rightarrow \quad \text{M} - \text{R}
\]
Cationic Curing Mechanism

CATIONIC CURING - UV
Initiation (Light & Heat)

\[ \text{photoinitiator} \quad \xrightarrow{h \nu} \quad \text{initiation} \]

\[ \text{initiation} \quad \xrightarrow{H^+\text{MF}_6^-} \quad \text{reaction} \quad \xrightarrow{\text{h} \nu} \quad \text{product} \]
Common Photoinitiators

Photocleavage - Type I

1-hydroxycyclohexyl phenyl ketone

2-hydroxy-2-methyl-1-phenyl-propan-1-one
Sulphonium Salt Cationic Photoinitiators

\[ X = \text{PF}_6^- \text{ or SbF}_6^- \text{ counterion} \]
Oligomers

bisphenol A diglycidyl ether diacrylate

aliphatic urethane diacrylate
Oligomers

Acrylated Acrylic

\[
\begin{array}{c}
\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH} \quad \text{C}=\text{O} \\
\text{O} \quad \text{O} \quad \text{O} \\
\text{R} \quad \text{R}' \quad \\
\text{CH}_2 \quad \text{CH}_2 \quad \\
\text{CH}-\text{OH} \quad \text{C}=\text{O} \\
\text{CH}_2 \quad \text{CH}_2 \\
\text{O} \quad \text{C}=\text{O} \\
\text{CH} = \text{CH}_2
\end{array}
\]
Film Formation in Powder Coatings
Film Formation in Powder Coatings

There are two major classifications of powder coatings, Thermoplastic and Thermosetting.

Thermoplastic powders melt and flow with the application of heat.

PVC, Nylon, Polypropylene, Vinyl, and Fluorinated resins

Thermosetting powders

Epoxy, polyester, polyurethane, and acrylic and combinations thereof.
A finely ground mixture of ingredients in a resinous base, which are solid at the time of application, but melt, flow, and coalesce into a protective film in the presence of heat.
Radical Curing Powder Coating

R + \text{C}-\text{C}=\text{O}\rightarrow R-\text{C}-\text{C}=\text{O}

R-\text{C}-\text{C}=\text{O} + \text{C}-\text{C}=\text{O}\rightarrow R-\text{C}-\text{C}-\text{C}=\text{O}

M \rightarrow \text{M-M}

M \rightarrow \text{M-R}
UV Cured Powder

- These powders follow a combination of conventional and UV cured systems.
- The melt and low is accomplished by a brief exposure to a heat source.
- The cure and cross linking is achieved by a brief exposure to an ultraviolet light source.

This technology is suitable for powder coating temperature sensitive materials such as wood products (MDF).
Challenges

- Highly pigmented systems are slow to cure
- Film thickness limitations
- Balance of good flow and cure is critical
- Line-of-Site
Film Formation

Applied powder

Or other source

IR

Melt and flow

UV (395-445 nm) 2000-4000 mJ/cm²

Finished wood
Film Formation in Coatings

References


Adhesion Aspects of Polymeric Coatings, J. Baghdachi, FSCT, 1997

Thank You!